

A META-ANALYSIS OF MERCURY LEVELS IN LAVACA BAY TEXAS

A Thesis

by

MARIA C. PILLADO

Submitted to the Office of Graduate and Professional Studies of Texas A&M University
and the Graduate Faculty of The Texas A&M University – Corpus Christi
in partial fulfillment of the requirements for the joint degree of

MASTER OF SCIENCE

Chair of Committee,	Paul Montagna
Committee Members,	Greg Stunz
	Jennifer Pollack
	David Evans
Head of Department,	Joe Fox

May 2014

Major Subject: Marine Biology

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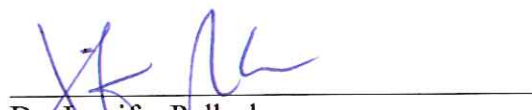
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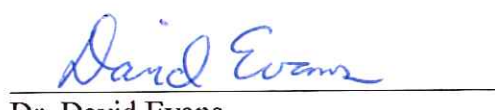
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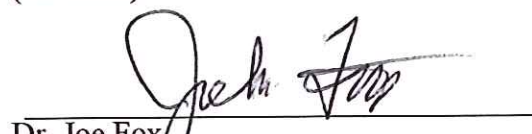
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Abstract

META-ANALYSIS OF MERCURY LEVELS IN LAVACA BAY TEXAS

Maria C. Pillado, B.S. Environmental Science, Texas A&M University-Corpus Christi

Chair of Advisory Committee: Dr. Paul Montagna

Lavaca Bay is a secondary bay to Matagorda Bay on the central Texas Coast. In 1970 Texas Department of Health (TDH) closed parts of Lavaca Bay to the harvesting of oysters due to mercury contamination as a result of contaminated wastewater discharged into the bay by a chlor-alkali plant operated by Alcoa. In 1988 TDH closed the area around Dredge Island which is adjacent to the chlor-alkali plant to the taking of finfish and crabs due to elevated mercury levels. In 1994 it was proposed that the area around Dredge Island and area around the chlor-alkali plant were placed on the National Priorities List (NPL). In December of 2001 the Record of Decision (ROD) was signed to initiate the remediation process.

The purpose of this study is to use a meta-analysis to determine if the mercury levels in secondary and tertiary trophic levels have changed between years 1992 and 2012, and if the levels in red drum (*Sciaenops ocellatus*) and oysters (*Crassostrea virginica*) have decreased over time. The meta-analysis used biota and sediment collected and analyzed for total mercury in 2012, historical data from Texas Department of Health (TDH), U.S. Environmental Protection Agency (EPA), and Woodward-Clyde (1992).

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Introduction

Mercury is an element with the atomic number of 80. It is a transition metal with many qualities. Mercury is the only metal that is liquid at room temperature. Elemental mercury has a high conductivity, low resistance, a constant rate of expansion and has the ability to form amalgams or alloys with various metals (King 1957, Schroeder & Munthe 1998). Mercury compounds have anti-bacterial and anti-fungal properties (King 1957, Wisniak 2008, Grandjean et al. 2010). These properties made mercury a sought after element for the past 2500 years (King 1957, Wisniak 2008). Mercury also has many negative health impacts on humans and other animals (Clarkson 2002).

Mercury exists in various forms. Mercury is mined from mercuric sulfide (HgS) which is a mercury ore called cinnabar (King 1957, Schroeder & Munthe 1998, Wisniak 2008). Elemental mercury (Hg^0) exists as a silvery white metallic liquid which will evaporate at room temperature (King 1957, Clarkson 1998, Schroeder & Munthe 1998, Wisniak 2008, USEPA 2011a). Elemental Hg also exists in a monovalent form (Hg^{+1} or Hg(I)) and a divalent form (Hg^{+2} or Hg(II)) (Clarkson 1998, Schroeder & Munthe 1998, Liu et al. 2011). Mercury forms both organic and inorganic compounds. Examples of inorganic compounds are mercuric sulfide (HgS), mercuric oxide (HgO) mercuric chloride (HgCl_2). These compounds are referred to as mercury salts. Examples of organic mercury compounds are ethyl mercury chloride and methyl mercury chloride (MeHgCl) (Syversen & Kaur 2012).

Mercury has a long history of uses over the past 2500 years. In 384-322 B.C. Aristotle coined the term quicksilver to describe mercury, because of the liquid and

silvery appearance (King 1957, Wisniak 2008). The ability of mercury to easily form amalgams with precious metals such as silver and gold, made it valuable during the 12th century for mining (Wisniak 2008). Mercury was also used during the 19th century gold rush in the western United States (Clarkson 2002, Alpers et al. 2005) and is still used for gold mining in the Amazon River Basin (Clarkson 2002) and other parts of the world often without regulation or oversight (UNEP 2013).

The high conductivity and low resistance of mercury has made it valuable in electro-chemistry. The resistivity of mercury is low and precisely reproducible and has been used as an international standard (King 1957). Mercury cathodes were useful in the production of chlorine and sodium hydroxide (Evans & Engel 1994, Frumkin et al. 2001, Wisniak 2008, UNEP 2013). The use of mercury cathodes lead to the contamination in Lavaca Bay, Texas

Mercury was used in the Ruben Dry Cell battery, which was developed during World War II. This battery was the precursor to today's miniature batteries and was also the beginning of the well-known battery company Duracell (Hintz 2009). The high conductivity, mobility and constant rate of expansion made mercury useful for measuring of temperature and pressures (King 1957, Wisniak 2008). It is currently used in various electrical switches and electronics devices (Wisniak 2008, UNEP 2013). Mercury is also used in energy efficient florescent light bulbs (UNEP 2013).

Mercury has a history of being used for medicinal purposes. In the 9th century Arabic physicians used mercury in ointments to treat eye and skin infections (Wisniak 2008). Elemental mercury was used to treat various digestive ailments and is still used in folk medicine today (Clarkson et al. 2003, Wisniak 2008). In the 16th century mercury

was used to treat syphilis (Clarkson 1998, 2002, Clarkson et al. 2007, Wisniak 2008, Grandjean et al. 2010, Bose-O'Reilly et al. 2010). Mercuric chloride (HgCl_2) was a commonly used antiseptic (King 1957, Clarkson 2002, Clarkson et al. 2003, 2007, Bose-O'Reilly et al. 2010, Syversen & Kaur 2012). The wide spread use of mercury in teething powders was determined to be the cause of the childhood disease Acrodynia in the 1950's (Dathan 1954, Clarkson 1998, Clarkson et al. 2003). The use of mercury in teething powders is now banned in the United States (Clarkson et al. 2003, Holmes et al. 2009, Syversen & Kaur 2012). Thimerosal, which is an organic mercury compound, is currently used in some vaccines as a preservative. There is ongoing debate to the safety of this compound and the level of exposure to children through vaccinations (Clarkson 2002, Clarkson et al. 2003, Zahir et al. 2005, Holmes et al. 2009, Bose-O'Reilly et al. 2010) . Dental amalgams also contain mercury and are actively used in the United States (Clarkson 1998, 2002, Wisniak 2008, Bose-O'Reilly et al. 2010, Syversen & Kaur 2012).

The toxic effect mercury on humans has a long documented history. In 1665 scholars wrote of the visible effects of mercury on miners mining mercury ore (HgS) commonly referred to as cinnabar (Wisniak 2008). The work hours for workers were cut from 16 hours to 6 hours to minimize the exposure to mercury (King 1957, Wisniak 2008). During the 19th century hatters making felt hats also showed symptoms of mercury poisoning. The term "mad as a hatter" was coined and the effects of mercury poisoning were depicted in the book "Alice in Wonderland" by the character The Mad Hatter (Clarkson 1998, Emanuel 2010) These incidents of elemental mercury poisoning resulted from the inhalation of mercury vapors. In 1863 in a chemical laboratory, methyl mercury (MeHg) was synthesized. Two lab personnel died after a sealed bottle of methyl mercury

was dropped on the laboratory floor (King 1957, Clarkson 2002, Clarkson et al. 2003, Wisniak 2008).

Methyl mercury has been the source of several mass poisonings (King 1957, Clarkson 2002, Wisniak 2008). The first event was in Minamata, Japan during the 1950's. Mercury contaminated industrial waste water was discharged directly in to Minamata Bay. The marine life in the bay became contaminated with methyl mercury. The main protein source for the residents of Minamata was seafood. The consumption of the contaminated seafood resulted in the poisoning thousands of residents (King 1957, Schroeder & Munthe 1998, Clarkson 2002, Clarkson et al. 2003, Wisniak 2008, Emanuel 2010).

In 1971 a mass poisoning occurred in Northern Iraq. The government ordered large quantities of grain for people who were starving in Northern Iraq. Due to an error, the grain which was intended for human consumption was treated with a fungicide containing methyl mercury. The people used this treated grain to make flour and bread, as a result 6530 of people were sickened and 459 people died (Clarkson 1998, Clarkson et al. 2003).

The toxicity of mercury compounds depend on their chemical form. Inorganic mercury compounds accumulate in the kidneys and liver. This can result in kidney failure and death. These compounds may also lead to some autoimmune diseases (Clarkson 1998, Zahir et al. 2005, Clarkson et al. 2007, Syversen & Kaur 2012). Inorganic compounds such as mercuric chloride have been used in cosmetics products, antiseptics and teething powders (King 1957, Clarkson et al. 2003, Bose-O'Reilly et al. 2010). The widespread use of inorganic compounds in these items has declined over the years. The

use of mercury compounds in cosmetics and teething powders are banned in the United States (Clarkson 2002, Clarkson et al. 2003, Wisniak 2008, UNEP 2013).

Organic mercury compounds are all toxic, but methyl mercury is considered the most toxic (Clarkson 1998, Morel et al. 1998, Zahir et al. 2005, Syversen & Kaur 2012). Methyl mercury is a lipophilic compound with an affinity towards bioaccumulation. Unlike other mercury compounds there is a delay in the onset of symptoms (Clarkson 1998, 2002, Syversen & Kaur 2012). The symptoms of methyl mercury poisoning include; ataxia, narrowing field of vision, muscle weakness, numbness in extremities, and impaired speech and hearing. In extreme cases it can cause paralysis, insanity, and eventually death. Methyl mercury can also cross the placenta interfering with the neurodevelopment of the fetus resulting in lower IQ, impaired motor skill development, cognitive development and function (Clarkson 1998, Clarkson et al. 2003, Syversen & Kaur 2012, UNEP 2013).

All the mechanisms that cause methyl mercury poisoning are not fully understood. It can pass through cellular membranes easily and can also cross the blood brain barrier. There is loss of cerebellar granule neurons, which disrupts the function of the cerebellum. The cerebellum is the area of the brain responsible for maintaining posture and balance, cognitive motor skills, and coordination of motor movements (Clarkson 1998, Syversen & Kaur 2012). Exposure to methyl mercury can be through inhalation, where approximately eighty percent of the methyl mercury is absorbed into the body. It can be absorbed through intact skin at a rate less than inhalation. Methyl mercury that is ingested results in up to one hundred percent absorption through the intestine (Clarkson et al. 2003, Syversen & Kaur 2012). Ingestion of contaminated

seafood is the most common form of methyl mercury exposure (Clarkson et al. 2003, Holmes et al. 2009, USEPA 2011a, UNEP 2013).

Methyl mercury accumulates in different concentrations throughout the body. Brain tissue has a strong affinity for methyl mercury; as a result the concentrations are usually three to six times higher than the body. As the body eliminates methyl mercury, the rate of elimination is slower in the brain. The liver and kidneys also have a slightly higher methyl mercury burden than the rest of the body (Clarkson 1998, Syversen & Kaur 2012). Methyl mercury can transport through the placenta to the fetus and fetal blood concentration can be higher than the mother's blood concentration, making methyl mercury exposure a concern for woman of child bearing age (Clarkson 1998, Syversen & Kaur 2012).

Methyl mercury also has negative effects on wildlife. Species that are piscivorous or consume animals that consume piscivores are most at risk for exposure to methyl mercury (Clarkson 2002, Emanuel 2010). This exposure can cause reduced fertility, slower growth, abnormal behavior that may affect survival and may result in death (Clarkson 2002, Emanuel 2010, Jakimska et al. 2011). Jakimska et al. (2011) summarized the effects of various metals on marine organism. Mollusks exposed to methyl mercury may experience peroxidation of lipids and formation of DNA adducts which affects cell metabolism. Methyl mercury adversely affects fish by disruption of the endocrine and reproduction systems. This can lead to problems with interspecific communication, reproduction, osmoregulation, and prey location (Jakimska et al. 2011).

Mercury is introduced in the environment through natural sources such as geothermal activities. It also outgasses from soils, and water bodies. Anthropogenic

sources of mercury come from the combustion of fossil fuels, gold mining, municipal and medical incinerators, and chlor-alkali production being the largest global contributors of mercury. Other sources include the municipal and medical incinerators, landfills, cement and paper production (USEPA 1997, UNEP 2013). The United States Environmental Protection Agency has passed laws to reduce mercury emissions and discharges in the United States under the Clean Air Act and Clean Water Act (EPA 2013).

The majority of mercury released into the environment is released into the atmosphere. Once in the atmosphere it has a residence time of up to one year. This allows for mercury to travel far from the original source of mercury release (Schroeder & Munthe 1998, Clarkson 2002). Approximately 98% of the mercury in the atmosphere is elemental mercury (Hg^0). Hg^0 is oxidized to one of the two oxidation states, mercuric (Hg^{+2}) or mercurous (Hg_2^{+2}) also referred to mercury (II) and mercury (I) respectively. The exact mechanisms for the oxidation of atmospheric mercury are not known.

Elemental mercury has a slow rate of oxidation. Once it is oxidized it then attaches itself to particulate matter and is deposited on the earth's surface. This process is called dry deposition. Mercury (II) can easily dissolve in water allowing for it to fall to the earth's surface through rain events. This process is called wet deposition (Morel et al. 1998, Schroeder & Munthe 1998, Liu et al. 2011, UNEP 2013). The highest levels of wet deposition in the United States occurs in the southeastern region (Schroeder & Munthe 1998).

Mercury is either directly deposited in marine estuaries or it is transported from runoff into rivers then in to the marine systems (Liu et al. 2011). Once in estuaries, mercury can be converted into methyl mercury by microorganisms or through abiotic

processes. This allows for the methyl mercury to become bioavailable to the food chain where it then biomagnifies and leads to bioaccumulation in top predators of the marine food web (Morel et al. 1998, Schroeder & Munthe 1998, UNEP 2013).

The abiotic process of mercury methylation is not fully understood. The rate and significance of methylation of mercury through an abiotic process is still under debate (Morel et al. 1998, Celo et al. 2006, Liu et al. 2011). The process requires methyl donors to be present. Reagents thought to methylate mercury are small organic compounds such as methyl iodine and methyl di-sulfide, while some larger compounds such as fluvic and humic acids also methylate mercury (Weber 1993, Morel et al. 1998, Celo et al. 2006). In addition to methyl donors the abiotic process depends on pH, salinity, form of mercury present and ionic strength (Weber 1993, Morel et al. 1998, Celo et al. 2006, Liu et al. 2011).

The biotic process of mercury methylation is a more widely studied process of mercury methylation in marine environments (Liu et al. 2011). The process occurs largely through sulfate reducing bacteria (SRB) and iron reducing bacteria (FeRB). Not all SRBs and FeRBs methylate mercury. The rate at which SRBs and FeRBs methylate mercury vary between species and depends on environmental conditions such as temperature, pH, availability of nutrients and electron acceptors, as well as the structure of the microbial community. The exact mechanism of mercury uptake by SRBs and FeRBs is not exactly known (Morel et al. 1998, Liu et al. 2011).

Once methyl mercury is in the marine aquatic environment it can either be de-methylated or taken up by various organisms. Methyl mercury can be de-methylated by either biotic or abiotic processes. Biotic de-methylation is achieved by mercury resistant

bacteria (MRB). The primary abiotic process is photo-degradation, but this process occurs primarily in the water column (Morel et al. 1998, Liu et al. 2011).

In addition to methylation and de-methylation, the oxidation of $\text{Hg}^{(0)}$ to Hg(II) and the reduction of Hg(II) to $\text{Hg}^{(0)}$ are important steps in the mercury cycle. Hg(II) can be reduced by biotic processes or abiotic processes. Evidence suggests that only Hg(II) and its compounds can be methylated by SRB and FeRB (Liu et al. 2011). Hg(II) and $\text{Hg}^{(0)}$ can both be methylated through abiotic processes but this methylation has only been simulated in a laboratory. It is unclear if this type of methylation occurs in the field (Weber 1993).

Once Hg(II) is reduced to $\text{Hg}^{(0)}$ it can either volatilize and enter the atmosphere or it can be oxidized and become available for methylation (Morel et al. 1998, Liu et al. 2011). All the mechanisms in the mercury cycle are not fully understood (Liu et al. 2011). What is known is that mercury is converted to methyl mercury in estuaries and it biomagnifies within organisms and bioaccumulates within food webs.

The most common pathway for human exposure to methyl mercury is through ingestion of contaminated seafood. Texas is home to 2.9 million recreational fishermen according to a 2001 joint governmental agency report (U.S. Department of the Interior et al. 2001). It is likely that this number has increased. The consumption of contaminated seafood poses a health risk to humans, especially at risk populations, such as women of child bearing age, pregnant women, or young children (USEPA 1997, UNEP 2013).

Study Site

Lavaca Bay is a secondary bay adjacent to Matagorda Bay, located along the central coast of Texas. It is a shallow bay with an average depth of 2.1 meters and an area of approximately 64 square miles (Britton & Morton 1989). The bay receives freshwater inflow from the Lavaca and Navidad Rivers. Wetlands, marshes and oyster reefs are found throughout the bay. Lavaca Bay is used for commercial and recreational fisheries, as well as industrial uses (USEPA 2001). The bay has a dredged ship channel with a depth of 11.6 meters to accommodate shipping traffic (USEPA 2001). Figure 1 provides a map of the study site.

In 1948 Alcoa began operating an aluminum smelter plant on the eastern shore of the bay. The smelter plant suspended operations in 1980. Bauxite refining began in 1958 and is still active. In 1962, Alcoa started an aluminum fluoride plant. This plant is currently functioning and producing aluminum fluoride and C-30 Hydrate, which is a fire retardant (Alcoa inc 2012). From 1966-1970 Alcoa operated a chlor-alkali plant. The plant used mercury cathodes in the manufacturing process. This process produced wastewater that was contaminated with mercury. This contaminated wastewater was transferred to settling ponds onto Dredge Island, where it sat for a period before being discharged directly into Lavaca Bay (USEPA 2001).

Dredge Island was built up with dredge spoils from the construction of the Alcoa ship channel and is located adjacent to the plant. The island has been used for gypsum disposal, dredge material disposal and waste water settling ponds for the chlor-alkali plant. The island was contaminated with mercury contaminated wastewater and mercury contaminated dredge spoils. The area around the island is also contaminated from direct

discharge of mercury contaminated wastewater and run off from contaminated soils (USEPA 2001).

In 1970 Texas Department of Health (TDH) closed parts of Lavaca Bay to the harvesting of oysters. TDH found the levels of mercury to exceed the Food and Drug Administration (FDA) threshold of 0.5 ppm in oysters, finfish and crabs. TDH only had the authority to restrict the harvesting of oysters at that time. The estimated rate of mercury enter Lavaca Bay at this time was approximately 30 kg per day from 1966-1970. This rate was reduced to 6 kg per day in 1970 (Bergquist et al. 1995). The oyster ban was lifted in 1971 when mercury levels dropped below the FDA threshold of 0.5 ppm (USEPA 2001). Currently the FDA has a threshold of 1.0 ppm (USEPA 1997).

In 1988 TDH closed the area around Dredge Island, which was adjacent to the former chlor-alkali plant, to the taking of finfish and crabs due to mercury levels. In 1993 it was proposed that the area around Dredge Island and area around the former chlor-alkali plant be placed on the National Priorities List (NPL). The two areas were placed on the NPL in 1994. In December of 2001 the Record of Decision (ROD) was signed. In 2011 the remediation dictated by the Record of Decision was completed (USEPA 2001).

History of Remediation

The primary source of mercury contamination in Lavaca Bay was from the contaminated waste water that was discharged into the bay. The ROD found secondary sources of mercury contamination (USEPA 2001). Runoff and erosion from Dredge Island was a source of continued mercury contamination. Sediment along the ship channel adjacent to the chlor-alkali plant was also a source of continued contamination.

This sediment was frequently re-suspended due to shipping and tug boat activities. Ground water from the underneath the chlor-alkali plant was found to be contaminated with mercury and leaching into Lavaca Bay (USEPA 2001).

1998-2001 Alcoa reinforced Dredge Island to prevent erosion and survive severe storm events, because the island would be the confinement area for contaminated soils. In 1999 Approximately 80,000 cubic yards of sediment were dredged and disposed of on Dredge Island and capped to prevent further contamination. The removal of sediments along the channel adjacent to the chlor-alkali plant removed and estimated 2300 pounds of mercury. The sediment in this area was frequently re-suspended due to shipping activities, therefore making the mercury in the sediment bioavailable and prevented natural recovery of the sediments (USEPA 2001).

The contamination of the bay through ground water was addressed with a ground water system that reversed the gradient of the mercury contaminated ground water and has prevented between 0.4-90 pounds of mercury per year from entering the bay. Sediments that were not in an area of frequent re-suspension were allowed to naturally recover. This means that the contaminated sediments were buried by natural sedimentation that occurs in Lavaca Bay. The purpose is that with time contaminated sediments will be buried deep enough, with mercury-free sediments, to prevent re-suspension or biological activities from making the mercury bioavailable to the food web.

Methyl mercury is known to bioaccumulate within organisms and biomagnify within food webs. Methyl mercury makes up approximately 90% of total mercury in fish (Evans & Engel 1994, Atwell et al. 1998). The purpose of this study is to conduct a meta-

analysis using data collected in 2012, and historical data, from TDH, EPA (USEPA 2011b), Woodward-Clyde ("Biological data summary report 1992 Lavaca Bay, TX" 1993), to determine if there have been changes in mercury levels. This study will specifically determine if mercury levels in secondary and tertiary trophic levels have changed by comparing biota and sediment from 1992 and sample collected in 2012, and will also determine if levels in red drum and oysters have decreased over time within the closed area of Lavaca Bay.

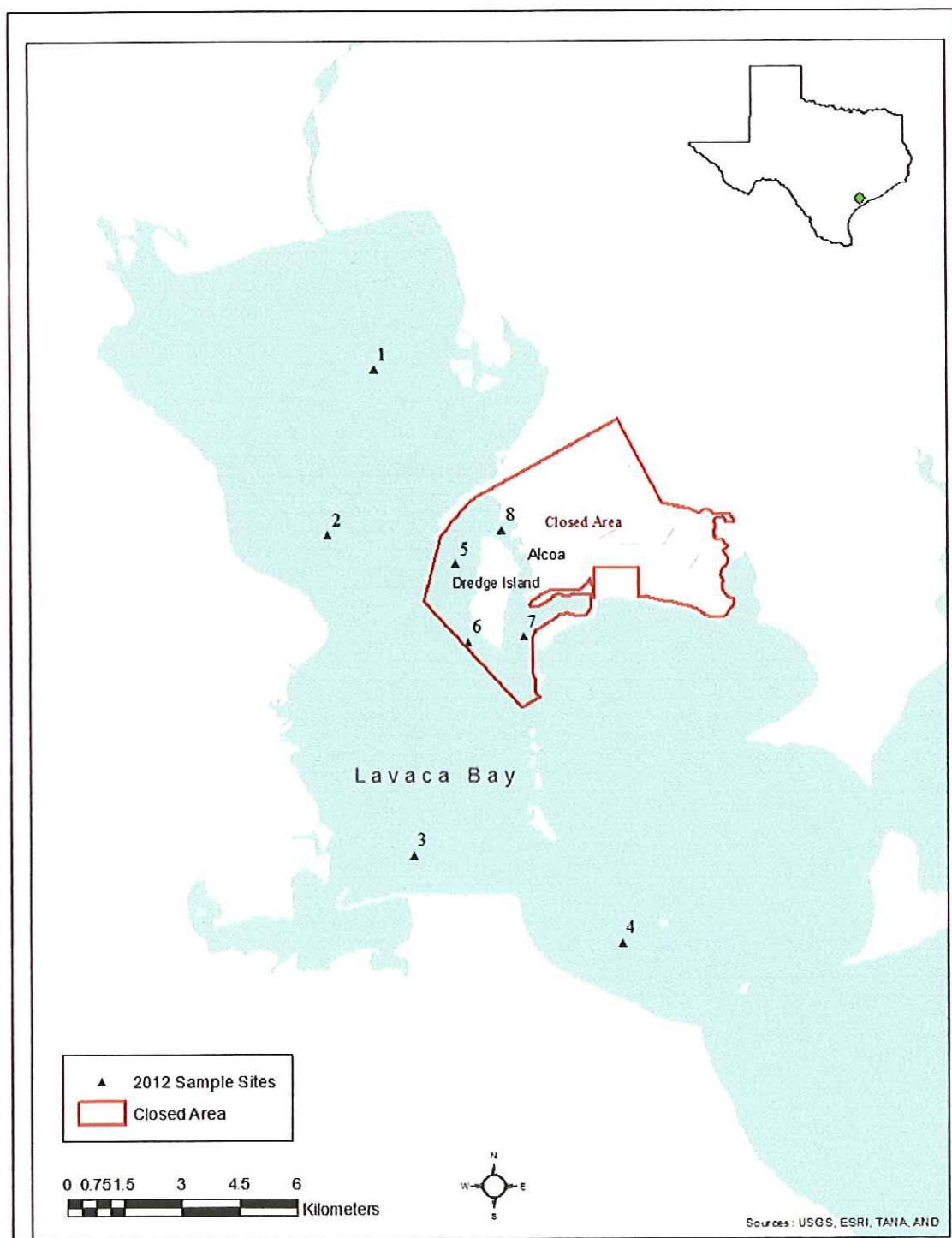


Figure 1 Map of Lavaca Bay, Texas with sample sites from 2012 and the closed area outlined

Materials and Methods

Sampling Design

For the samples collected in 2012, Lavaca Bay was divided into two areas, the closed area and the open area. The closed area is the waters around dredge island and adjacent to the former chlor-alkali plant, which is currently closed to the harvesting of finfish and crabs. Four sites were selected on the northwest, northeast, southwest and southeast sides of the island. The open area is the area that is not in the closed area. Four sites were selected starting from the northern part of the bay to the southern part of the bay (Figure 1)

In each area of the bay, four sites were sampled for sediment and biota. Various types of gear were used to sample each site. A trawl (21 ft in length with a 2 cm mesh) was used to capture invertebrates and small vertebrates. The trawl was pulled for an average of 15 min at 3.0 knots covering approximately 1667 m². A minimum of one pull with a maximum of 4 pulls was conducted at each open site. Gillnets were set at each site for 2 hours. The gill nets were 30 m long with two panels with a net size of 2.5 cm and 5.0 cm, respectively. These nets were used to capture larger fish. A small oyster dredge was used to collect live oysters from reefs. Hook and line were used with both live and artificial baits to target specific fish. Two sediment cores (7 cm in diameter) were taken per station to a depth of 7 cm, the top 3 cm of sediments were separated and analyzed.

A Hydrolab multiparameter sonde was used to measure temperature (°C), dissolved oxygen (mg/l), and salinity (psu), and a secchi disk was used to measure turbidity. Samples were taken in November of 2012. All samples were put on ice in the

field and transported to the laboratory. All biological samples and sediment samples were frozen in a -20° C freezer until processed

Mercury Analysis

All processing implements were cleaned with methanol and rinsed with de-ionized water to prevent cross contamination between samples and are referred to as “clean”. Each sample was wrapped in foil, which was pre-combusted in a muffle furnace at 450° C for 4 hours. The samples were placed in a zip-lock freezer bags, labeled and placed in a -20° C freezer until shipment NOAA Laboratory in Beaufort, North Carolina to be analyzed by Dr. David Evans. All samples were shipped overnight packed in dry ice.

Oysters (*Crassostrea virginica*) were shucked with shucking knives which were cleaned between samples to prevent cross contamination. Each oyster was wrapped in pre-combusted foil, labeled, put in a zip-lock bags. The exoskeleton was removed from shrimp. All shrimp were wrapped in pre-combusted foil, labeled, and placed in a zip lock bags and all samples were placed in a -20° C freezer until shipped for analysis.

All fish with the exception of bay anchovies (*Anchoa mitchilli*), were filleted with clean knives. Dorsal muscle tissue was removed and wrapped in pre-combusted foil, labeled, placed in a zip lock bag and placed in -20° C freezer. All samples remained frozen until shipment for analysis

Total mercury analysis was performed using a modified EPA method 7473 “Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry”. Total mercury concentrations were measured

using a Milestone DMA-80 mercury analyzer. Tissue samples were weighed out in quartz sample boats to a target weight of 0.20 g and analyzed without further processing. Quality assurance samples included two reference materials. The first reference material was National Research Council of Canada (NRCC) lobster hepatopancreas reference material for trace metals (TORT-2) and the second was NRCC dogfish liver certified reference material for trace metals (DOLT-3). The quality assurance measurements during mercury analysis were good. The accuracy, recoveries of the certified reference materials (CRMs) TORT-2 and DOLT-3 were $112\% \pm 2\%$ and $99\% \pm 2\%$ respectively. Duplicate sample analysis showed coefficients of variation averaging 1%.

The meta-analysis was comprised of four datasets which were analyzed. The datasets were comprised of three historical data from TDH, EPA, Woodward-Clyde and data collected in 2012. This data was used in part and combined to perform analysis. The purpose was to determine if there was an effect on mercury levels due to remediation. Statistical analysis was performed with the statistical program R Project for Statistical Computing (R Core Team 2012)

Results

The first analysis was of oyster (*Crassostrea virginica*) data which combined TDH historical data, 2012 data, and Woodward-Clyde. The data had various sample sizes. (Table 1) The purpose of this analysis was to compare the change in mercury levels over time. Data were not present for every year but spanned the time frame 1970-2012. Table 1 lists the years data was collected and the average mercury level for that year and area.

Figure 2 plots the mean mercury levels for each year for both open and closed areas of Lavaca Bay.

Table 1 Mean annual mercury concentration (ppm) in oysters Lavaca Bay Texas

Year	Open Mean Hg	Standard Deviation	Number Sampled (n)	Closed Mean Hg	Standard Deviation	Number Sampled (n)
1970	0.40	+/-0.29	98	2.93	+/-1.8	27
1971	0.19	+/-0.09	91	0.39	+/-0.12	19
1972	0.17	+/-0.06	28	0.26	+/-0.07	5
1973	0.17	+/-0.04	2	0.20	+/-0.08	3
1974	0.09	+/-0.04	4	0.15	+/-0.05	7
1975	0.09	+/-0.04	4	0.15	+/-0.04	3
1977	0.13	+/-0.05	12	0.14	+/-0.04	3
1980	0.07	+/-0.05	4	N/A		
1984	0.06	+/-0.006	4	N/A		
1988	N/A			0.12	+/-0.04	8
1992	0.06			0.20		
1993	N/A			0.10	+/-0.02	3
1994	N/A			0.11	+/-0.01	2
1996	N/A			0.19	+/-0.04	2
2012	0.06	+/-0.02	11	0.09	+/-0.009	5

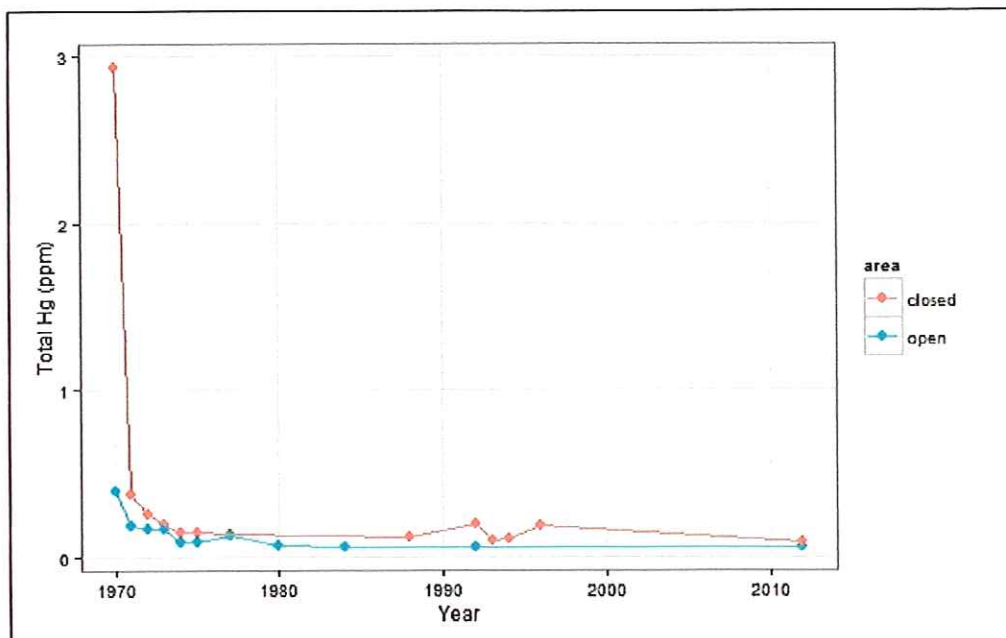


Figure 2 Mean mercury concentrations (ppm) in oysters Lavaca Bay Texas

The highest levels of mercury in oysters in both the closed area and open area were found in 1970. The open area oysters had an average level of 0.40 ppm of total mercury and the closed area had an average level of 2.93 ppm. In 1971 levels declined more than in any other year. The open area oysters declined from 0.40 to 0.19, while oysters in the closed area declined from 2.93 to 0.38. In 2012 there was only a 0.03 ppm difference between the closed area and the open area.

The second analysis was of red drum (*Sciaenops ocellatus*). This dataset comprised total mercury levels in red drum for the open and closed areas, from years 1970-1996. Data were not present for all years for both areas. Woodward-Clyde was added for the year 1992, because TDH had no data for that year.

The purpose of this analysis was to determine if there was a difference in bioaccumulation in red drum between the closed area and the open area. An ANCOVA was run using total mercury as the dependent variable, area and year as the independent

variables and length was the covariate. A significant p-value of <0.0013 was determined for the interaction term (Table 2). The Tukey-Kramer was used to adjust for multiple comparisons the null hypothesis for this test was the least square means for both the closed area and the open area are equal. The p-value was significant p-value <0.001 (Table 3)

Table 2 Table of ANCOVA results for red drum in Lavaca Bay from 1980-1996

Source	Degrees of Freedom	Sum of Squares	F Value	Pr>F
Year	15	18.59	2.41	0.0028
Length	1	2.508	4.88	0.0281
Area	1	0.038	0.07	0.7850
Length*Area	1	5.457	10.62	0.0013
Error	240	123.345	0.514	

Table 3 Least square means, adjustment for multiple comparisons: Tukey-Kramer for ANCOVA for red drum for 1980-1996.

Area	Least Square Mean for Hg	Pr> t
Closed	1.533	<0.001
Open	0.176	

This analysis did not comprise the full TDH dataset because there was only length data available for 1980-1996. Woodward-Clyde data was used for 1992 because TDH did not have data for that year.

The next analysis of red drum used data from TDH, EPA, and Woodward-Clyde to determine if there was a decline in the mean levels of mercury in red drum from 1977-2010. Linear regression was used to determine if there was a significant change. The p-value was <0.001 , R-squared was 0.36 and the slope was -0.052 (Figure 3).

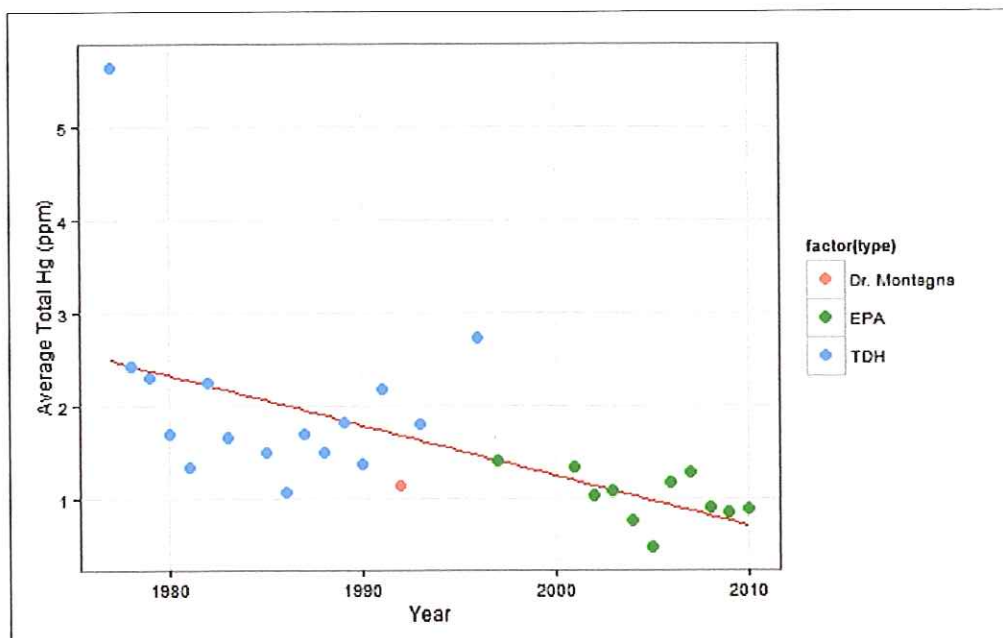


Figure 3 Linear regression of mean mercury levels in red drum tissue per year in the closed area of Lavaca Bay with the outlier

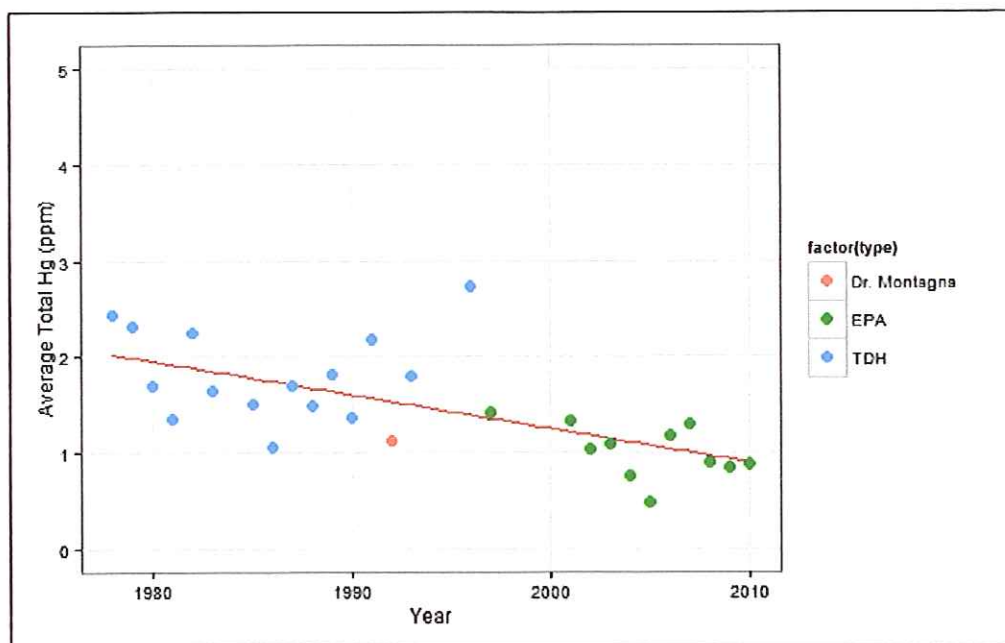


Figure 4 Linear regression of mean mercury levels in red drum tissue per year in the closed area of Lavaca Bay without the outlier

Table 4 Mean mercury levels in red drum fish tissue in Lavaca Bay Texas

Year	Open Mean Hg	Standard Deviation	Number Sampled (n)	Closed Mean Hg	Standard Deviation	Number Sampled (n)
1970	0.78	N/A	1	N/A		
1971	0.80	N/A	1	N/A		
1977	N/A			5.65	+/-0.07	2
1978	0.89	+/-1.31	8	2.43	+/-0.86	16
1979	N/A			2.31	+/-	
1980	N/A			1.70	+/-0.82	21
1981	N/A			1.34	+/-0.71	10
1982	0.38	+/-0.14	11	2.25	+/-1.16	11
1983	N/A			1.65	+/-0.55	12
1985	N/A			1.50	+/-0.01	3
1986	N/A			1.06	+/-0.43	7
1987	N/A			1.70	+/-0.86	4
1988	0.43	+/-0.64	12	1.49	+/-0.60	15
1989	N/A			1.82	+/-0.59	3
1990	N/A			1.37	+/-0.76	15
1991	0.46	+/-		2.18	+/-1.10	4
1992	0.21	+/-0.09	15	1.13	+/-0.819	73
1993	0.31	+/-0.09	16	1.80	+/-1.27	9
1996	0.28	+/-0.14	8	2.73	+/-1.14	5
1997	0.51	N/A	N/A	1.42	N/A	N/A
2001	0.49	N/A	N/A	1.33	N/A	N/A
2002	0.64	N/A	N/A	1.03	N/A	N/A
2003	0.48	N/A	N/A	1.09	N/A	N/A
2004	0.47	N/A	N/A	0.76	N/A	N/A
2005	0.48	N/A	N/A	0.87	N/A	N/A
2006	0.43	N/A	N/A	1.17	N/A	N/A
2007	0.65	N/A	N/A	1.29	N/A	N/A
2008	0.40	N/A	N/A	0.90	N/A	N/A
2009	0.38	N/A	N/A	0.85	N/A	N/A
2010	0.38	N/A	N/A	0.88	N/A	N/A

The first data point from 1977 was a statistical outlier with a Cook's distance of greater than 1. The outlier had a sample size of only two (Table 4). A linear regression was performed with the outlier removed (Figure 4). The R-squared was 0.43 and the p-value was <0.001 and the slope was -0.038.

The fourth analysis was to determine if there was a significant difference between areas and between years 1992 and 2012 in lower trophic level organisms and sediment. The trophic level range for this dataset was between 2.00 and 2.99. The trophic level was estimated by Wrast (2008). Wrast used stomach content analysis and stable isotopes from tissue to determine the trophic levels in Lavaca Bay (Wrast 2008).

Samples collected in 1992 were compared with samples collected in 2012. Species caught and analyzed are listed in Table 6. Sediments were treated as a species for the purpose of this analysis. A two-way block ANOVA was run with species as the blocking factor. A natural log transformation was performed on the dependent variable, total mercury, to improve normality of residuals. There was significant difference between years, where 1992 was higher than 2012 in both the closed and open areas. There was a significant difference between the two areas where the open area was less than the closed area. The interaction term between year and area was not significant (Table 5).

Table 5 ANOVA results for mercury concentration in 6 species and sediments between area (open and closed) and year (1992 and 2012).

Source	Degrees of Freedom	Sum of Squares	F Value	Pr>F
Area	1	1.619	23.112	<0.0001
Year	1	0.584	8.337	0.0064
Species	7	21.804	44.458	<0.0001
Area*Year	1	0.053	0.755	0.3859

Table 6 Number of species compared in both areas in 1992 and 2012 in Lavaca Bay Texas.

Species	1992 Open	1992 Closed	2012 Open	2012 Closed
Croaker <i>Micropogonias undulatus</i>	5	0	2	0
Gafftop <i>Bagre marinus</i>	14	0	1	0
Hardhead <i>Ariopsis felis</i>	5	6	1	1
Menhaden <i>Brevoortia patronus</i>	5	15	3	5
Oysters <i>Crassostrea virginica</i>	12	39	11	5
Spot <i>Leiostomus xanthurus</i>	0	5	10	1
White Shrimp <i>Litopenaeus setiferus</i>	26	0	16	0
Sediment 0-3 cm	4	6	3	8

Mercury levels have declined over time. The mean annual concentration of mercury in oysters declined dramatically between 1970 and 1971, immediately after cessation of direct discharge of mercury containing wastes to the bay. The levels in red drum have declined gradually over the past three decades. Secondary and tertiary trophic

levels from 1992 and 2012 showed that there was a decline in the level of mercury between 1992 and 2012 but, mercury concentrations in the closed area has not declined to levels in the open area.

Discussion

Efforts to stop the direct contamination of Lavaca Bay began in 1970 when, mercury pumped in to the bay at a rate of approximately 30 kg per day from 1966-1970, was halted (Bergquist et al. 1995). In 1970 TDH found elevated levels of mercury in oysters (USEPA 2001). It was after this finding that the rate of mercury being directly discharged in to the bay was reduced to 6 kg per day (Bergquist et al. 1995).

The average level of mercury in oysters declined from 2.93 to 0.38 ppm in 1971. This was the largest decline in levels of mercury within the closed area of Lavaca Bay. Oysters do not bioaccumulate mercury in the same manner as fish (Cunningham & Tripp 1975, Palmer et al. 1993). In a study conducted by Palmer et al. (1993), oysters were taken from closed area of Lavaca Bay and transplanted into an adjacent uncontaminated bay, and oysters from the uncontaminated bay were placed in the closed area of Lavaca Bay. It was found that the oysters in Lavaca Bay had a depuration rate of up to 0.07 ppm of mercury per day in the uncontaminated bay. It was also found that oysters placed in the contaminated area readily accumulated mercury (Palmer et al. 1993).

The rapid depuration/accumulation rate in oysters coupled with the fact they are sessile allows them to be good indicators of the water quality within a contaminated area like the closed area. Oyster feed on suspended matter in the water column (Cunningham & Tripp 1975, Palmer et al. 1993). The rapid decline in the mercury level in oysters

between 1970 and 1971 is likely do to the cessation of mercury being pumped directly into the bay.

The largest decline in mercury for oysters in the open area was also between 1970 and 1971. While the level in oysters did not exceed the FDA action level of 0.5 ppm there was a decline of 0.21 ppm. The closed area of Lavaca Bay does have some physical barriers that partial separate it from the open area of the bay, but there is no part of the closed area that is totally separated from the open area. It is likely that wind and currents carried some of the mercury outside of the closed area. While the levels in oysters in the open area were not at the FDA action level they were highest in 1970 and declined in 1971 also. In 2012 the level of mercury in the oysters in the closed area was similar to the level in the open area with a difference of 0.03 ppm. This indicates that the mercury is not currently in the water column at a concentration that is different from the open area.

The next species evaluated was the red drum. This species was chosen because it is an upper trophic level predator (Scharf & Schlicht 2000) and there were abundant data available over an extended period of time.

There was a decline in mean levels of red drum from 1977-2010. A similar analysis was done by Sager (2002) where the linear regression analysis only included years up to 1996. The slope was -0.050 with the outliers removed (David R 2002). This was similar to my analysis which included years 1997-2010 in which the slope was -0.038 with the outliers removed. The differences in slopes can be attributed to the addition of data in the later analysis. There is variation that is not accounted such as fish length, location of capture. This variation could be the cause of the differences in slopes.

Another cause could be the amount of mercury bioavailable. There were significant remediation activities that took place during 1977-1999. These activities dramatically reduce the amount of mercury entering Lavaca Bay. It is possible the mean levels that are seen in red drum after 1999 are result of residual mercury and not active contamination.

The largest decline in mercury levels for red drum in the closed area was from 1977-1978. Unfortunately there was no data available before 1977. After 1978 the decline was at a slower rate. Mean mercury concentration for 1977 was 5.64 ppm. This number is a statistical outlier. It may be possible that it is a true value; however it represented only two fish. There is a positive relationship between total length and the age of red drum (Scharf 2000). This analysis did not take into account length or age in this dataset because total length was not available for all the datasets and fish age was not available for any of the datasets. The accuracy of the rate of decline may be greatly affected by this missing data. The rate could be greater or it could be less depending on the size of red drum caught and averaged.

The second analysis of red drum data used the TDH dataset, which was used to determine if there was a difference in bioaccumulation between the open area and the closed area of Lavaca Bay. The TDH dataset only had total length available from 1980-1996. Woodward-Clyde dataset also had total length data available for 1992 and was added to the dataset. An ANCOVA was used to determine if bioaccumulation was significantly different between the open and closed area.

The analysis showed that there was a significant difference between the closed and open area. There was a greater variation in the closed area verses the open area. The closed area makes up only a small portion of Lavaca Bay (Figure 1).

There are seagrass beds, oyster reefs and underwater structures in and near the closed area. These areas are frequented by red drum as feeding grounds. The close proximity of the feeding grounds to the closed area means that is possible for the fish to feed in both the open and closed area without having to leave the vicinity in search of food. It is also possible that a fish could get all or most of its food items from the closed area. Fish frequenting the feeding grounds in the open area near the closed area also have a higher probability of being caught in the closed area even though it is not their primary feeding grounds. This would explain how there were many fish caught in the closed area that had mercury levels close to those found in red drum caught in the open area. Fish with the highest levels of mercury could be fish that spend the majority of their time feeding in the closed area

The open area of Lavaca Bay is much larger than the closed area. There was less variation in mercury levels in the fish caught in the open area. This can be explained partially by the location of feeding grounds. There are several areas far from the closed area that could provide red drum with all the prey items needed thus not requiring them to spend the energy to swim to the closed area in search of prey. The location of capture was not factored into this analysis due to lack of data, however it could explain some of the variation in both the closed and open areas.

There is a seasonal component in the red drum diet which was not factored into the analysis (Scharf & Schlicht 2000). Many prey items can move into and out of the open and closed area. Wrast (2008) found that the food web in Lavaca Bay changed seasonally. In Galveston Bay red drum feed on different prey seasonally (Scharf & Schlicht 2000). Since there was a lack of data in regards to when red drum were sampled the seasonal component could not be analyzed.

The significant difference in bioaccumulation suggests that there is some site loyalty in the feeding grounds of the red drum. If there were no site loyalty then we would expect that there would be high variation in the open area as well as in the closed area of Lavaca Bay, due to the fact that red drum would travel the distances to the open area sites on the other side of the bay to feed.

The final study was of organisms in the secondary and tertiary trophic levels and sediment. For the purpose of this analysis sediment was analyzed with the organisms to determine the overall change between 1992 and 2012. There was a significant difference between 1992 and 2012. There was also a significant difference between areas. The mercury concentrations in these organisms has declined between 1992 and 2012 which indicates that there is some recovery occurring. The significant difference between the open and closed area indicates that levels have not declined to that of the open area.

One species that was not evaluated was blue crab (*Callinectes sapidus*). Blue crab is a seasonal prey item for red drum (Scharf & Schlicht 2000). The data available indicated that blue crab varied greatly in annual averages from 1970-1996. This data did not take into account the size of the crabs for years before 1980. Additional information

available through the EPA(USEPA 2011b) only had data for juvenile blue crabs. These differences prevented accurate comparisons for mercury levels in blue crabs over time. It should be noted that the mercury levels in juvenile blue crabs have declined between 1997-2010 (USEPA 2011b).

Cessation of active pumping of mercury into the bay may be the remediation action that contributed most to the decline in mercury levels in both oysters and red drum. After the active pumping of mercury was decreased the level of mercury in oysters declined. Levels of mercury in red drum also declined at a rate less than the oysters. Remediation efforts were made in 1996-2001 to prevent active contamination of Lavaca Bay through contaminated ground water and contaminated soils eroding into the bay. Removal of some of the contaminated sediment to prevent it from becoming bioavailable to the food web (USEPA 2001). These remediation efforts may have also had an effect on the decline in the mercury levels of the lower tropic level organisms between 1992 and 2012.

Mercury is a naturally occurring element, but it can also be a persistent contaminate(USEPA 1997, Emanuel 2010, Liu et al. 2011, UNEP 2013). Mercury poses a threat to human health, especially to children (USEPA 1997, Clarkson 1998) Remediation efforts have reduced the amount of mercury that enters Lavaca Bay, and the levels of mercury within organisms have declined over time. The decline of mercury in sediments has been slower than predicted (USEPA 2011b). In a 1997 study of sediment deposition rates, it was estimated that the half-time for mercury recovery for sediments in the closed area of Lavaca Bay was 6 +/-1 year (Santschi et al. 1999). The model assumed that there was not sources of active contamination entering the closed area, and

sedimentation rates were based on the rates from 1960-1997 (Santschi et al. 1999). The rates of sedimentation may have changed with the changes in fresh water inflow into Lavaca Bay this could be a factor in why the recovery in Lavaca Bay did happen at the rate predicted

The future of Lavaca Bay is trending towards the reduction of bioavailable mercury entering the food web. An area of concern is the stability of Dredge Island. The island is where the contaminated sediments from dredge activities are stored. The island has been re-enforced and capped to prevent the recontamination of Lavaca Bay (USEPA 2001). It was noted that there were some minor problems with the retaining wall and mild erosion (USEPA 2011b). The maintenance of this island and the island's ability to maintain its structural integrity during a major storm event may be the biggest concern for Lavaca Bay. If the containment systems on the island were to fail there could be a reintroduction of mercury into Lavaca Bay. Since mercury has negative impacts on humans and animals (Clarkson 1998, Jakimska et al. 2011) it is important to continue monitoring Lavaca Bay to ensure mercury is not being reintroduced in to the bay and that mercury concentration in biota continue to recover.

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